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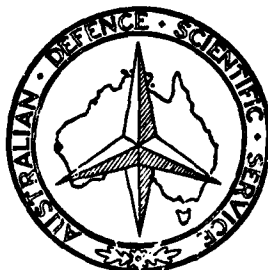
DEFENCE STANDARDS LABORATORIES

MARIBYRNONG, VICTORIA

REPORT 522

THE PASSIVATION OF NICKEL-BASE THERMOCOUPLE ALLOYS

AND SOME RELATED TOPICS

N. A. Burley

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DEPARTMENT OF SUPPLY

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DEFENCE STANDARDS LABORATORIES

REPORT 522

THE PASSIVATION OF NICKEL-BASE THERMOCOUPLE ALLOYS AND SOME RELATED TOPICS

N. A. BURLEY

SUMMARY

This report describes the scientific research aspects of an overseas visit to England, Sweden, Norway, and the USA, which was made in June, 1971, in connection with the DSL Research Project on Highly Stable Nickel-Base Alloys for Thermo-couples.

The overall objects of the visit were:

1. To attend and present two papers (1, 2) at the Fifth Symposium on Temperature held at the National Bureau of Standards, Washington, D.C., from 21st to 24th June, 1971.

2. To confer with Research Directors of the major thermocouple alloy manu-facturing firms on technical and commercial problems arising in the production of the new DSL-formulated nickel-base thermocouple alloys 'Nicrosil' and 'Nisil'.

3. To confer with overseas experts on some advanced and complex aspects of the high-temperature oxidation of nickel-base alloys.

Aspects of the visit related to 1. the Fifth Temperature Symposium and 2. the commercial production of Nicrosil and Nisil are the subjects of previous reports (3, 4). The present report concerns 3. the scientific aspects of the visit, in particular the progress of some current overseas researches into certain aspects of the gas-reactivity and passivation of refractory alloys generally similar in type to the nickel-base thermocouple alloys presently under investigation at DSL.

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ABSTRACT

This report describes the scientific research aspects of an overseas visit to England, Sweden, Norway, and the USA, which was made in June, 1971, in connection with the DSL Research Project on Highly Stable Nickel-Base Alloys for Thermocouples.

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The present report concerns 3., the scientific aspects of the visit, in particular the progress of some current overseas researches into certain aspects of the gas-reactivity and passivation of refractory alloys generally similar in type to the nickel-base thermocouple alloys presently under investigation at DSL.

CONTENTS:

THE PASSIVATION OF NICKEL-BASE THERMOCOUPLE

ALLOYS AND SOME RELATED TOPICS

1. INTRODUCTION

Previous work at DSL (5-9) has shown that the accuracy of
nickel-base thermocouples can be seriously impaired by two characteristic
types of change which occur in their temperature/thermoelectromotive force
characteristics, namely (i) a gradual and generally cumulative drift in
thermal emf on long exposure at high temperatures, and (ii) a short-term
cyclic change in emf on heating in the temperature range ca 250 to 550°C
(ca 525 to 825 K). This work has related the long-term thermal emf drifts
to the depletion of reactive solutes by oxidation, and the short-term
changes to short-range ordering.

In more recent work (10) it has been shown that the environmental
stability of nickel-base thermocouple alloys can be significantly enhanced
by increasing solute levels above those required to cause a transition from
internal to external modes of oxidation, and/or by selecting solutes which
preferentially oxidize to form impervious diffusion barrier films. The
short-term emf changes can be minimized by thermal-treatments which
stabilize the short-range order, or eliminated by the choice of solute
levels at which structure-dependent emf changes are not evident.

The formulation at DSL of two new thermocouple alloys, Nicrosil
(positive; Ni-15½Cr-1½Si)* and Nisil (negative; Ni-4½Si-1/8Mg), has
now been described (1). These alloys have been shown (1) to be much more
resistant to air oxidation and to have much higher thermal emf stabilities,
and hence accuracies, than existing nickel-base thermocouple alloys.

This report is concerned primarily with certain other means by
which the stabilities of Nicrosil and Nisil might be even further enhanced.
These are the establishment of a passivating layer, in the form of a
continuous surface film of a preferred oxide, by an initial thermal-treatment
under controlled conditions of temperature and oxygen pressure; and also
the addition, in trace quantities, of certain rare-earth and reactive
elements which are known to favourably affect oxidation behaviours in alloys
of similar types.

This report summarizes discussions which were held with certain
overseas workers who were currently conducting researches in topics bearing
on these two processes, and also on certain other relevant topics. Various
conclusions are drawn concerning the further development of Nicrosil and
Nisil.

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* All alloy compositions given in this report are expressed as percentages
by weight, unless otherwise indicated.

2. PASSIVATION TECHNIQUES

2.1 Preferential Oxidation

In the formulation of the new DSL thermocouple alloys Nicrosil (Ni-15½Cr-1½Si) and Nisil (Ni-4½Si-1/8Mg) (1,10), basic thermodynamic data was used to relate the conditions of solute content, temperature and oxygen pressure under which certain discrete and continuous oxide layers could form exclusively on the surface to produce highly effective diffusion-barriers. Using such factors as the standard free energies of formation and growth rates of the various oxides developed (NiO, Cr_2O_3, SiO_2), the alloy inter-diffusion coefficients, and the solubility and diffusivity of atomic oxygen in the alloys, it was possible to predict that in the case of Nicrosil the barrier would comprise two predominant layers - a Cr_2O_3 film superimposed upon an insulating SiO_2 film located at the metal/scale interface, whilst in Nisil the barrier would consist of a single surface layer of SiO_2.

That these diffusion-barrier oxide layers form as predicted and are, in fact, highly efficient oxidation inhibitors has been established by recent studies (1,10). These studies also showed that Nicrosil/Nisil possess very much higher environmental and thermoelectrical stabilities than conventional nickel-base thermocouple alloys, up to about 1250°C (about 1525 K) in air.

It has been observed (1), however, that the greater part of the long-term thermal emf drift which occurs in the new DSL thermocouples at high temperatures takes place in the very early stages of exposure. This suggests that the oxide films, once established, greatly inhibit diffusion, but that in the early stages their formation is relatively slow and/or is characterized by departures from the theoretically predicted conditions of steady-state oxide growth. Opportunity was therefore taken whilst overseas to discuss the initial (transient) oxidation of certain nickel-base alloys, generally similar in type to the new DSL alloys, with certain workers who were currently investigating these aspects.

Wood(1)* discussed his current studies of the early stages of oxidation of certain binary nickel-base alloys in 1 atm (100 kPa) oxygen at 600°C (873 K). He has shown that with Ni-Cr, Ni-Al, and Ni-Si, significant amounts of NiO are produced before the steady-state predicted healing-layer of the particular less-noble metal oxide is formed at the scale base. Wood's collaborator, Whittle (2), elaborated upon these results. In the case of Ni-Cr, NiO was always the major oxide formed in the transient stages of oxidation of Ni-5.6 and 11.1 at.-%Cr, with increasing amounts of $NiCr_2O_4$ forming as oxidation proceeded. The Cr_2O_3 healing-layer did appear, however, soon after exposure. The amount of Cr_2O_3 forming increased with chromium content and was detectable as early as 2 to 5 min with Ni-22.0 at.-%Cr. The establishment of the passivating Cr_2O_3 layer was most rapid at grain boundaries, presumably because the

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* Italic numbers in parentheses refer to 'Conferees' - ref. Appendix A

diffusivity of chromium ions there is greater than it is in the bulk alloy. Whittle felt that the increase in chromium in Nicrosil to 15½ wt.-% from the conventional 9-3/4 wt.-% level would result in a greatly increased transient passivation rate, the effect being more marked the finer the grain size. In the case of Ni-7.3 at.-%Si, both NiO and SiO_2 (α - quartz) predominated in the early stages of oxidation. The thinness of the oxide layer at all stages suggested, however, that the SiO_2 healing-layer was very rapidly established.

Wood opined that although the author had correctly interpreted the effects of the various thermodynamic factors he had used to predict the steady-state scaling characteristics of Nicrosil/Nisil, he should also take into account that on initial exposure very small impinging nuclei of all the simple component oxides and more complex oxides did, in fact, form simultaneously on the metal surface, irrespective of the various free energies of formation and initial growth rates involved. This factor had to be taken into account in determining the morphology of the transient oxides formed at the metal/scale interface, particularly if it was desired to predict the interfacial ionic diffusivity relative to that of the bulk of the oxide layer formed at steady state.

It appeared from these discussions that the diffusion inhibiting propensity of the Cr_2O_3 and SiO_2 films forming as steady-state passivating layers on Nicrosil and Nisil could be deleteriously affected by the co-formation of NiO at the transient oxidation stage.

The author subsequently discussed with both Wood and Whittle his proposal that the transient formation of NiO on Nicrosil and Nisil could be suppressed by an initial thermal-treatment under certain controlled conditions of temperature and oxygen pressure which were favourable to the exclusive formation of Cr_2O_3 and/or SiO_2. Both workers agreed that the theoretical basis proposed by the author for the suggested passivation treatment appeared to be sound. This basis is outlined in the next paragraph for the case of Ni-Cr-Si (which includes Nicrosil) but is equally applicable for the case of Ni-Si (which includes Nisil).

If Ni-Cr-Si is heated in an abundant supply of air, the three components of the alloy will oxidize at different rates which are dependent initially upon the differences in the standard free energies of formation of their respective oxides. If however the oxygen potential of the reacting gas is progressively lowered, say by reducing its total pressure or by changing its composition, the selective oxidation of chromium with respect to nickel, and of silicon with respect to both chromium and nickel, is enhanced. This means that the oxidation of nickel can be suppressed whilst that of chromium and silicon continues, next the oxidation of nickel and chromium can be suppressed whilst that of silicon continues, and finally the oxidation of all three alloy components can be suppressed. Such a lowering of the oxygen pressure will also lead, successively, to the dissociation of any NiO, Cr_2O_3, and SiO_2 already formed. Fig. 1, which has been calculated from heats of decomposition and entropy data, shows the partial pressure of oxygen in equilibrium with the relevant oxides of nickel, chromium, and silicon, at temperatures up to $1000^{\circ}C$ (1273 K). If the partial pressure of oxygen and the temperature are such that conditions correspond to the area marked A, the atmosphere will be oxidizing to all three reactions. If, however, the condition lies around B it will be seen

that the oxygen partial pressure has fallen below the equilibrium pressure for the reaction -

$$2NiO \rightleftharpoons 2Ni + O_2$$

and thus the equilibrium

$$K = C\left[Ni\right] \times P_{O_2}/C\left[NiO\right]$$

is disturbed by a lowering of P_{O_2}, and a decrease in $C\left[NiO\right]$ will occur to restore the equilibrium, i.e. the reaction will go to the right and no oxidation of nickel will occur. The oxygen partial pressure is, however, greater than the equilibrium value for the reactions -

$$2Cr_2O_3 \rightleftharpoons 4Cr + 3O_2, \text{ and}$$

$$SiO_2 \rightleftharpoons Si + O_2,$$
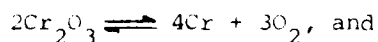
both of which will accordingly go to the left and the oxidation of chromium and silicon only will take place. When the condition lies around C both the nickel and chromium reactions will go to the right and the exclusive oxidation of silicon will take place. When the condition lies around D all three reactions will go to the right and the surface will remain bright. From Fig. 1, it will further be seen that at any given partial pressure, increasing the temperature brings the condition closer to the equilibrium state and will thus tend toward the suppression of one reaction and the enhancement of the selective effect.

Thus, in theory, the deleterious effects of the initial formation of NiO in transient oxidation can be eliminated by preliminary thermal-treatments at controlled temperatures and pressures in which the exclusive formation of Cr_2O_3 and/or SiO_2 would occur. This could involve lowering the oxygen pressure to around D in Fig. 1, at some suitable temperature, and raising it again to around C, or B, as appropriate.

This passivation proposal was discussed with several other workers. Fleetwood (5) and Parry (6) thought that the very low oxygen pressures required might possibly be attainable in argon/oxygen mixtures, but warned that the data of Fig. 1 apply only to equilibrium conditions and that actual values under the practical conditions they proposed were likely to be removed somewhat from those shown. Douglass (3) further pointed out that data of the kind presented in Fig. 1 gave little indication of the kinetics of the reactions, and these would also result in deviations in practice from equilibrium conditions. All agreed, however, that the proposal seemed inherently capable of practical realization, optimum working conditions being readily determinable from

experiments based on the data of Fig. 1.

Kofstad (9) indicated that Moreau and Benard (11) had shown that in the bright annealing of Fe-Cr and Ni-Cr the conditions for dissociation of Cr_2O_3 could readily be achieved with mixtures of hydrogen and water vapour according to the reaction -

$$2Cr + 3H_2O \rightleftharpoons Cr_2O_3 + 3H_2$$

Their results for Ni-Cr are summarized in Fig. 2, which suggests that the temperature dependence of the reaction

$$2NiO \rightleftharpoons 2Ni + O_2$$
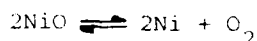
is not as great under these conditions as the thermodynamic data in Fig. 1 predict.

Edwin (2) felt that the proposal was of considerable commercial significance to the field of high-temperature alloys in general and to thermocouple alloys in particular. In industrial practice it would be necessary to maintain close control over the three variable factors temperature, composition and absolute pressure of the reacting gas. His firm (Bulten-Kanthal) is experienced in this type of process control of protective atmospheres for such processes as bright annealing, and could probably adapt such expertize to the passivation of drawn thermocouple wires. Individual thermocouples could, in similar manner, be passivated by the user.

2.2 Trace Element Additions

It has long been recognized that the presence of small quantities of rare-earth elements, as well as other active elements such as yttrium and scandium, in refractory alloys significantly improves both their isothermal and thermal-cycling oxidation resistance, especially in the vital area of scale adhesion. Until recently, however, there has been little understanding of this important effect in refractory alloys including nickel-base thermocouple alloys.

Numerous hypotheses (e.g. 12, 13) have been advanced to explain how these trace additions affect the oxidation kinetics and scale adhesion of such alloys; the most significant of these are -

   (i)   the formation of an oxide of the reactive metal at
         the oxide/metal interface;

(ii)   increased diffusion of desirable elements by changing
         the properties of the base-metal (alloy), such as
         expanding the lattice by the addition of elements
         with larger atomic volume;

(iii)   formation of a convoluted alloy/oxide interface or
         preferential oxidation at grain boundary intersections
         with the scale producing improved adherence of the
         oxide layer (sometimes called the "key-on" effect);

(iv)   the ability of internal oxide particles to act as
         vacancy sinks and adsorb inwardly flowing vacancies,
         thus preventing void formation at the alloy/oxide
         interface; and

(v)   improvement of sintering and plasticity of the oxide
         scale in the presence of rare-earth element oxides.

          It appears that there is no single mechanism by which rare-earth
and reactive element additions improve the high-temperature oxidation
resistance of nickel-base alloys.   Generally, the most accepted
explanation has been the key-on effect, which was originally considered to
improve the oxide adherence only by tenuous internal oxide formation.
However, according to Wood (1) the convoluted alloy/oxide interface is now
emerging as a more important factor.   What is certain is that in the case
of Nicrosil and Nisil the efficacy of the diffusion inhibiting films Cr_2O_3
and SiO_2, and hence thermo-emf stability, can be significantly improved by
the judicious addition of reactive elements to these alloys.   Of those
elements already tried, namely cerium, zirconium and magnesium, all have
proved to be most effective, in particular magnesium.

          Opportunity was taken whilst overseas to discuss the progress of
certain current researches in this field with various workers who were
seeking to define more precisely the mechanisms by which these trace elements
produced their beneficial effects.   It was hoped that some insight would
be gained into the bases for selection of the most suitable reactive element
additions for Nicrosil and Nisil.

          Kvernes (10) described his recent studies of the role of yttrium
in the high-temperature oxidation of five Ni-(2 to 9)Cr-6Al alloys with
yttrium additions between 0.005Y and 0.7Y in the temperature region 800
to 1200°C (1073 to 1473 K) in oxygen pressures of 1, 10 and 720 torr (0.13,
1.33, and 100 kPa).   Kvernes found that the yttrium improved the oxidation
behaviours of these alloys and generally the addition of 0.1Y and 0.2Y
gave most improvement.   The oxidation kinetics were found to indicate
asymptotic scale growth with time.   This, he suggested, was due to the
formation of sub-grains in the alloy which provide enhanced diffusion of
aluminium out to the surface, and increase the number of oxide nucleation
sites.   Additions of more than 0.3Y resulted in preferential grain
boundary oxidation and a convoluted alloy/oxide interface (key-on).   This
effect, together with the formation of an aluminium and yttrium double
oxide, produced increased adherence of the $\alpha-Al_2O_3$ scale on these alloys.
It was most probable that a secondary beneficiating mechanism was sub-grain
refinement which occurred when 0.1Y to 0.2Y was present.   The enhanced
diffusivity of aluminium in the low-angle sub-grain boundaries probably

increased the rate of formation of the surface $\alpha\text{-Al}_2\text{O}_3$ film.

Of particular interest to DSL's thermocouple research project was Kvernes' reference to his current work on the effects of similar additions of yttrium to Ni-Cr alloys. Sub-grain refinement was also observed in these alloys, but the chief beneficiation appeared to be a keying effect produced by the formation of YCrO_3 where grain boundaries intersected the surface. A high melting point intermetallic compound Ni_5Y was observed in the grain boundaries as a micro-precipitate, but whether this contributed to the enhanced oxidation resistance of yttrium-bearing Ni-Cr alloys was yet to be determined.

Wood (1) presented some data arising from his recent investigations of the influence of the Group IIIA metals scandium, yttrium and gadolinium on the oxidation of Fe-15Cr and Fe-27Cr. These elements reduced the oxidation rates in both alloys considerably, the effects being more marked at longer times and higher temperatures. Scale adhesion was noticeably improved on thermal-cycling. Wood felt that these effects would have analogous counterparts in Ni-Cr thermocouple alloys. His opinions on how these elements enhanced the oxidation resistance in Fe-Cr can be summarized thus -

(i)   small particles of Group IIIA metal oxides in the substrate increase the alloy interdiffusion coefficient, probably due to enhanced sub-grain boundary diffusion;

(ii)   pure or mixed oxides (e.g. Y_2O_5 or YCrO_3) layers form at the alloy/scale (Cr_2O_3) interface and at grain boundaries near the interface; these ultimately interfere with outward diffusion of Cr^{3+} ions through the alloy and into the scale;

(iii)   the highly convoluted metal/scale interface, not evident in the binary Fe-Cr alloys, plays a major role in keying the surface oxides; and

(iv) Cr^{3+} ion diffusion in the oxide is retarded by solute interaction due to the ionic size effect.

Wang (28) drew the author's attention to the recent Russian investigations (14) into the oxidation rates of lanthanum-bearing Ni-Cr-Si heating-element alloys. The effect of the addition of 0.1 La to Ni-20Cr-(0.3 to 1.3)Si had been studied at 1000 to 1200°C (1273 to 1473 K) over exposure times up to 100 hr in air. This work is of considerable significance because of the similarity of the compositions of the alloys studied to Nicrosil. It showed that the oxidation rates of Ni-20Cr-1.3Si are very considerably reduced by the addition of lanthanum. As with Nicrosil at DSL, the Russian alloys formed scales containing silicon in the form of SiO_2 in the α-crystoballite modification. Of considerable significance to the ultimate development of Nicrosil is the fact that the passivating layer of SiO_2 appears on these alloys at much lower temperatures when lanthanum is present.

Armijo (4) referred to his participation in a current
investigation with Tien and Rand (15) into the effects of scandium and
yttrium on void formation in Ni-12Al during oxidation at 1200°C in air.
In the binary alloy the oxidation is characterized by the formation of a
non-adherent scale of γ-Al$_2$O$_3$, an internal oxidation reaction zone in which
the selective oxidation of aluminium occurred, and the formation of a
generous number of spherical cavities in the internal reaction zone. Armijo
thought that these cavities were Kirkendall voids, formed as a consequence
of the agglomeration of vacancies caused by the unequal diffusion of
aluminium ions toward the external scale and the diffusion of nickel ions
in the opposite direction. In the alloy containing 0.2Y, two major
differences were found after oxidation; namely the external scale was much
more resistant to spallation and the density of observable voids (> 1 um
diam) was negligibly small. Tien and Rand have reportedly concluded from
these results that one of the mechanisms whereby yttrium promotes oxide
adherence is by providing sinks for excess vacancies, which otherwise would
agglomerate at the oxide/substrate interface and form firstly voids and
ultimately cracks.

As stated above, it has already been shown at DSL that the
addition of one or more of the reactive elements cerium, zirconium and
magnesium in trace quantities to Nicrosil and Nisil markedly enhances their
environmental and thermoelectrical stability. In addition, it can be
concluded from the discussion summaries above that several other reactive
elements, in particular yttrium and lanthanum could have similar effects.
Further research would be needed to determine which of all these elements
produced the greatest benefit, and how and in what quantities they did so.

3. SOME RELATED TOPICS

In addition to the main emphasis on passivation topics, numerous
other matters of direct relevance to the Thermocouple Research Project were
discussed. A summary of the discussions on a few of these topics, chosen
by way of important example, follows:-

3.1 Effects of Silicon on the Oxidation of Ni-10Cr and Ni-20Cr

Armijo's (4) recent work on this subject was of direct interest,
as silicon is an important oxidation inhibiting component of both Nicrosil
and Nisil (1,10). As in the development of Nicrosil (Ni-15½Cr-1½Si) at
DSL, Armijo has also found that silicon additions to Ni-(10 and 20)Cr
substantially reduce the oxidation rate by means of a layer of SiO$_2$
(α-crystoballite) that forms at the oxide/metal interface. In Nicrosil,
silicon is not very effective unless present in quantity $\geqslant$ 1%. Armijo
found that in alloys containing 1Si the SiO$_2$ layers are discontinuous,
whereas in alloys containing 3Si the layers are continuous. He was
interested in the author's contention that a defect-free layer of SiO$_2$
could be formed by a transient passivation process such as is described
above, and he suggested that a Ni-15Cr alloy containing silicon in which
such a film was formed should show a very low oxidation rate; Ni and Cr

ions would be virtually insoluble in such a film and consequently there would be very little driving force (low chemical potential gradient) for the diffusion of these elements through it.

3.2 Exfoliation and the Mechanical Behaviour of Scales

One of the chief causes of loss of protective scales from refractory alloys is the build-up of strains due to volume mismatch, adherency, epitaxy, etc, and the resultant stresses that exceed the fracture stress of the scale. Even if strain-free scales form during isothermal oxidation, subsequent thermal-cycling may create strains due to differential thermal dilation of the oxide and the metal.

Douglass (δ) discussed his current views on how stresses in oxide films can be relieved. He believes that crystallographic slip, although possible, is not a dominant mechanism, but rather plastic deformation of either scale or substrate. He strongly emphasized the importance of creep and the influence of several variables such as point defects and their generation during oxidation. The author gained the impression that very little could be done to improve scale properties by reduction of stresses, although possibilities for this existed in -

(i)   the addition of sufficient alloying element to form an oxide that was both protective (low defect concentration) and had a coefficient of thermal expansion that is more nearly matched to that of the substrate;

(ii)   pre-oxidation at lower temperatures to form a fine-grained scale if Herring-Nabarro creep is desired to reduce stresses;   and

(iii)   pre-oxidation at higher temperatures if it is desired to eliminate porosity and the attendant loss of strength associated with it.

It is to be noted that in the selection of silica films to protect both Nicrosil and Nisil, factors (i) and (iii) are favourable and that the extreme thinness of the films (1) militates against the generation of high stress values.

3.3 Reactivity of Nicrosil with Atmospheric Nitrogen

A cause for concern in the development of Nicrosil was its possible high-temperature reactivity with atmospheric nitrogen. Whittle (2) and Fleetwood (5) both referred to some relevant findings in their recent joint investigation into the cyclic oxidation of Ni-(15 to 50)Cr. When chromium was sufficiently concentrated for the structure to contain the α_1 phase, this phase was preferentially attacked by nitrogen to form Cr_2N, which gave rise to substantial oxide penetration, due to chromium depletion, and to increased spalling. Attack on the α_1 phase by nitrogen

was more pronounced at the higher temperatures. From this work it seems that nitrogen reactivity with chromium will not be a problem in Nicrosil (15½Cr).

3.4 Reactivity of Nicrosil with Sulphur-Bearing Atmospheres

Albert (*38*) discussed the current investigations of Spengler (16) into the effects of sequential sulphidation and oxidation on the propagation of sulphur in Ni-15Cr. This work was relevant to the behaviour of Nicrosil in sulphur-bearing atmospheres. Spengler is proposing that the sulphidation of nickel-base alloys is a self-sustaining reaction in that once chromium sulphides are formed in the metal, subsequent oxidation of the sulphides can liberate sulphur and nucleate new chromium sulphide particles along an advancing front. He has investigated this proposal by exposing samples of Ni-15Cr (which had been presulphidized in an SO_2-N_2 mixture) to an O_2-N_2 mixture for up to 300 hr at 1600^OF (1145 K). A progressive inward migration of chromium sulphides was observed by optical microscopy. Chemical analysis showed the total amount of sulphur in the sample to be conserved even up to 300 hr of oxidation. Albert claimed that these results are consistent with the self-sustaining model:-

$$2Cr_3S_4 + 9\underline{O} \rightarrow 3Cr_2O_3 + 8\underline{S}$$

$$8\underline{S} + 6Cr \rightarrow 2Cr_3S_4$$
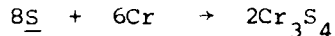
It may therefore be reasonable to assume that the sulphidation of a Ni-Cr thermocouple alloy could proceed self-sustainingly in atmospheres containing SO_2 and O_2. What remains to be seen is whether the protective film of SiO_2 on Nicrosil will "insulate" the alloy from the sulphur gases. In this regard, Albert advised the author to investigate the possibility of the formation of volatile silicon sulphide on Nicrosil when exposed in such atmospheres.

3.5 Oxide Dispersions in Thermocouple Alloys

The incorporation of dispersed oxides in Nicrosil and Nisil was first envisaged by the author as a means of improving the high-temperature strength and creep-resistance of these alloys without impairing their environmental and thermoelectrical stabilities. At first thought the addition of a thermoelectrically inert material, such as thoria or alumina, appeared promising.

In recent times, however, evidence has accumulated which suggests that oxide dispersions in nickel-base alloys can significantly enhance their oxidation resistance, quite apart from any strengthening effects. The phenomenon seems well established, for example, in more concentrated Ni-Cr alloys where oxide dispersions are known to promote the development of a continuous protective Cr_2O_3 layer, and furthermore, to reduce the growth rate of the layer. A question of importance is whether the phenomenon is active at the concentration at which chromium is present

in Nicrosil (15½Cr).

The recent investigations of Kvernes (10) into the oxidation behaviour of thoriated Ni-Cr alloys suggests that it is. He has studied the oxidation of Ni-(13.5 to 33.7)Cr-1ThO$_2$ alloys in flowing oxygen at 150 torr (20 kPa). He found that fine-grained substructures and associated dislocation densities, which are stabilized by the thoria particles, promote short-circuit diffusion of chromium in these alloys. The enhanced chromium diffusivity is responsible for -

(i)   the rapid formation of continuous Cr$_2$O$_3$ subscale beneath NiO duplex scale in the Ni-13.5Cr-1ThO$_2$ alloy, and

(ii)   a change in the growth mechanism for the selective oxide Cr$_2$O$_3$ in Ni-22.6Cr-1ThO$_2$ which produces an order of magnitude reduction in growth rate.

Kvernes claimed that Nicrosil (15½Cr), if thoriated, would oxidize as in (ii) above. He based this assertion on the fact that for Ni-13.5Cr-1ThO$_2$ the oxidation is sensitive to specimen surface preparation, illustrating that 13.5Cr is near the critical amount of chromium necessary to produce selective oxidation on these thoriated alloys.

Douglass (6) shared Kvernes' views in this matter. He discussed them in the light of the recent work of Giggins and Pettit (17) who investigated the effects of sub-surface dispersion of Al$_2$O$_3$ in Ni-(5 to 20Cr) alloys on their oxidation characteristics in 76 torr (10 kPa) oxygen pressure in the temperature range 900 to 1100°C (1173 to 1373 K). Giggins and Pettit claim that the oxidation rate of all alloys tested was generally reduced by the dispersions, and that Cr$_2$O$_3$ scales were formed to a greater or less degree in all cases.

Douglass was dubious as to whether the stabilizing influence of dispersed oxides would, in general, be so marked as to always extend to these more dilute Ni-Cr alloys. He referred to the current work of Stringer and Hed (18) who were studying, as part of a more general investigation of the effects of dispersed oxide phases on the oxidation of nickel and cobalt-base alloys, the effect of a dispersion of samaria, Sm$_2$O$_3$, on the high-temperature oxidation of Ni-7.5Cr over a wide range of oxygen pressures. Their results appear to indicate that dispersed samaria has no effect on the oxidation process in Ni-7.5Cr, which is somewhat contrary to the results of Giggins and Pettit for Al$_2$O$_3$.

It would seem, however, that a distinct possibility exists that an oxide dispersion in Nicrosil might improve both its oxidation resistance and its strength at high temperatures. It has already been established (1) that the internal/external oxidation transition composition for the exclusive formation of Cr$_2$O$_3$ on the surface of Nicrosil is somewhat less than its chromium content of 15½Cr. The singular advantage of an oxide dispersion in this alloy is that it would depress this transition composition to some lower level.

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APPENDIX A

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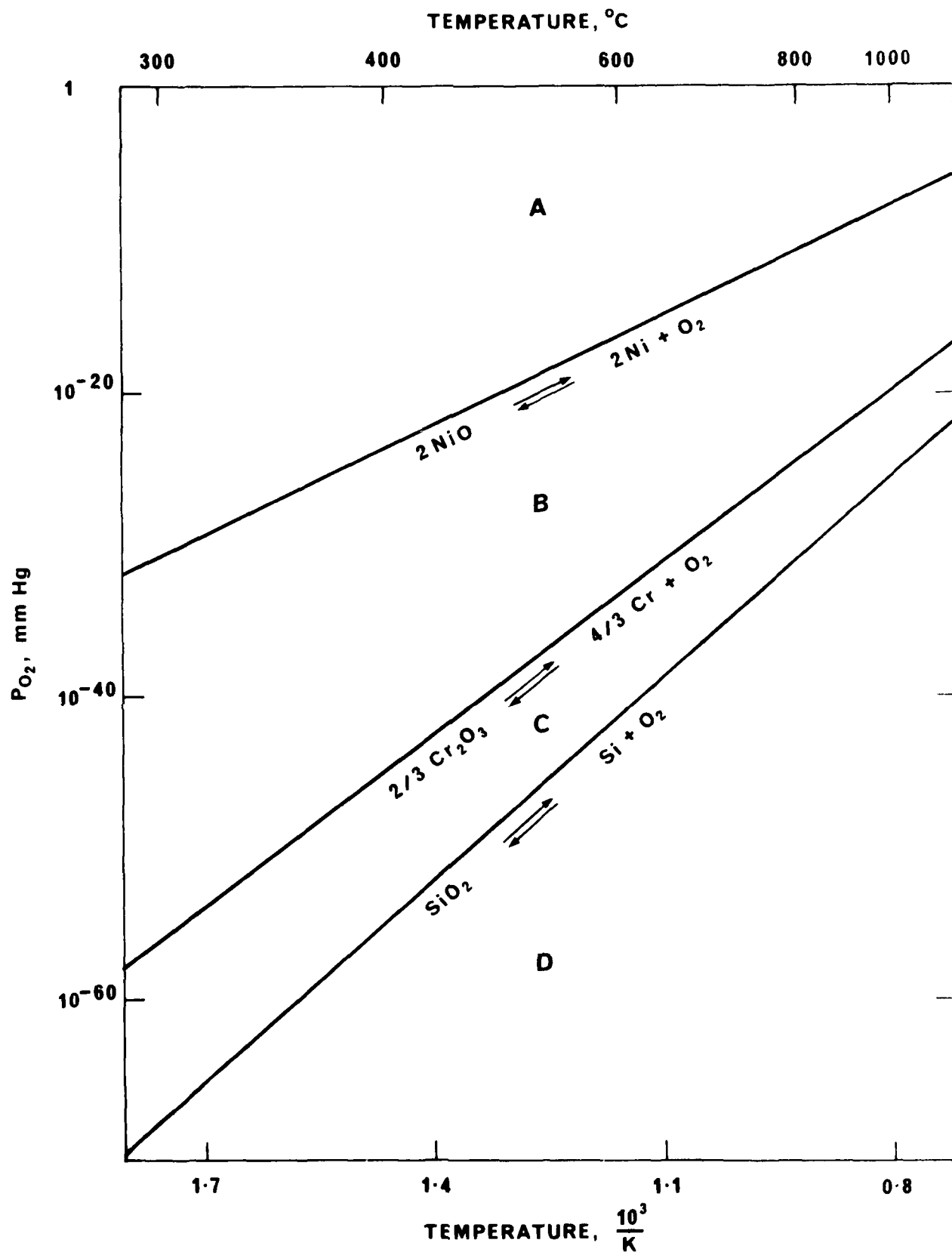43. Mr. W.F. Soleau, Assistant Manager - Sales

FIG. 1 — Reaction equilibrium : relation between P_{O_2} and temperature. 1 mm Hg = 133.3 Pa
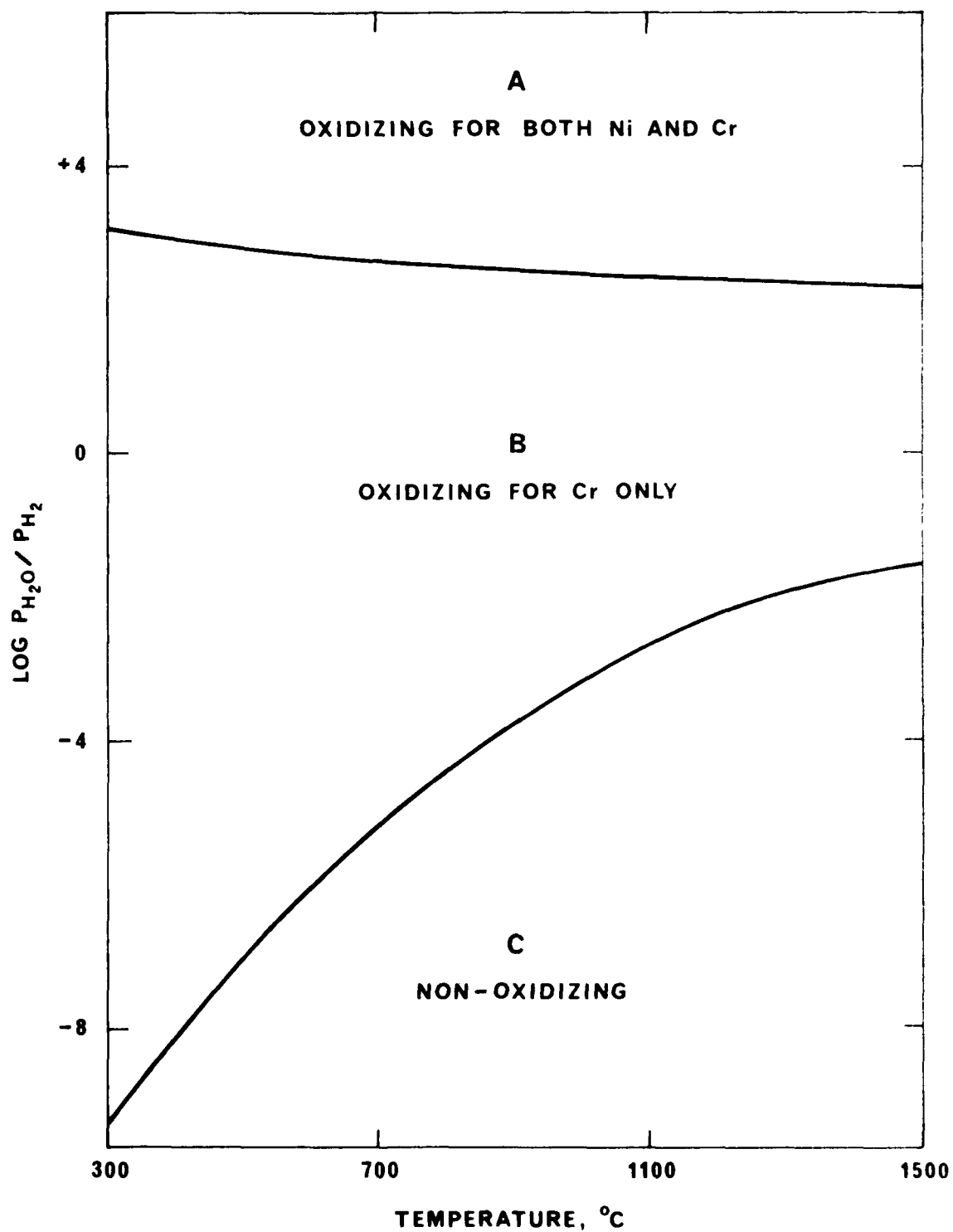
(For areas A to D, see text)

FIG. 2 - Relationship between log P_{H_2O}/P_{H_2} and temperature of oxidation of Ni-Cr in hydrogen/water vapour mixtures.

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